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Sensitization of Tio_2 Nanoparticles With Cobalt Phthalocyanine: an Active Photocatalyst for Degradation of 4-Chlorophenol Under Visible Light

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Abstract

In this work, preparation and visible light induced photocatalytic activity of sulphonated cobalt phthalocyanine complex sensitized TiO_2 nanoparticles (CoPcS-TNP) as photocatalyst for photocatalytic degradation of 4-chlorophenol (4-CP) has been reported. The study carried out using XRD, DRS, FT-IR, nitrogen physisorption and TEM techniques. Results revealed that TiO_2 nanoparticles possessed only the anatase phase with crystal sizes of about 7-10 nm. The doping amount of CoPcS remarkably affected the activity of TiO_2 nanoparticles as photocatalyst. Oxalic acid, pyruvic acid and malonic acid were the major intermediate species at the final stage of the degradation process as identified by gas chromatography-mass spectrometery.

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Keywords: TiO_2; Nanoparticles; Phthalocyanine; Degradation; 4-chlorophenol.

1. Introduction

How to improve the photocatalytic activity of TiO_2 in the visible region is the main focus of the recent TiO_2 photocatalysis research, Pelaez et al. (2012). Dye-sensitized photocatalysis begins with the light absorption of dye and a subsequent electron transfer from the excited dye to the conduction band of TiO_2. The use of dyes like phthalocyanines and porphyrins has attracted significant attention because of their low cost and efficiency relative to the conventional solid-state conversion of visible light into chemical energy. Incorporation of phthalocyanines into

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TiO_2 gel has also been reported. Ranjit et al. (1998), Wang et al. (2006), Zhang et al. (2006). Although these reports provide new insights in this field, due to the incomplete characterization and uncertain validation of the photocatalytic mechanism, complementary works is still needed. In this work, TiO_2-based photocatalysts containing different amounts of sulphonated cobalt phthalocyanine (CoPcS) were used for the photocatalytic degradation of 4-chlorophenol (4-CP) under visible light, which revealed enhanced photocatalytic activity as compared to the pure TiO_2. The reaction intermediates were identified by GC-MS.

2. Experimental

2.1. Photocatalysts preparation and characterization

TiO_2-based photocatalyst containing different amounts of CoPcS and pure TiO_2 were synthesized with little modification in the described procedure in ref, Zhang et al (2006). These photocatalysts are labelled as CoPcS-TNP(a), where (a) is the nominal weight percentage of CoPcS in the final solid. The synthesized samples were characterized by different techniques such as XRD, DRS, FT-IR, nitrogen physisorption and TEM.

2.2. Photocatalytic degradation monitoring

In a typical run, the suspension containing photocatalyst and 50 mL aqueous solution of 4-CP (40 mg/L) was stirred for 10min first in the dark to establish adsorption/desorption equilibrium. Irradiation experiments were carried out in a self-built reactor. In some experiments, H_2O_2 was also added to the solution as oxidant before light irradiation. A visible (Halogen, ECO OSRAM, 500W) lamp was used as irradiation source. At certain intervals, small aliquots (2 mL) were withdrawn and filtered to remove the photocatalyst particles. These aliquots were used for monitoring the degradation progress, with Biochrom WPA, Biowave II spectrophotometer at λ_{max}= 224 nm.

3. Result and discussion

3.1. X-ray diffraction analysis

The powder XRD patterns of the prepared samples are shown in Fig. 1. Their patterns clearly indicate that the synthesized TiO_2 and the photocatalysts have a pure anatase structure with all major peaks matching well with the standard pattern of bulk anatase (AMCSD 99-101-0679). The peaks positions and lattice parameters of anatase phase remain practically unchanged for TiO_2 and photocatalysts, supporting the structural integrity of the TiO_2 phase (Fig. 1). X-ray powder diffraction patterns of TiO_2 and photocatalysts show only peaks belonging to the anatase, suggesting that CoPcS is distributed on the semiconductor surface and not as separate phase.

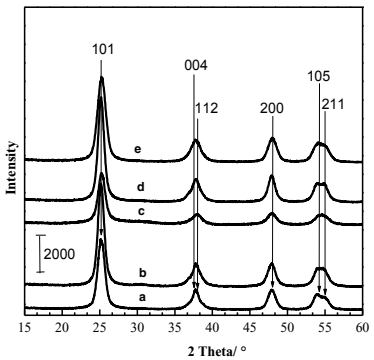

Fig. 1. Powder XRD patterns of (a) TiO_2; (b) CoPcS-TNP (0.56); (c) CoPcS-TNP (1.12); (d) CoPcS-TNP (2.24); and (e) CoPcS-TNP (3.36).

3.2. Diffuse reflectance analysis

Figure 2 shows the diffuse reflectance spectra of the synthesized samples. Because of the large band gap energy (3.1 eV), pure TiO_2 has no significant absorbance for visible light and exhibits only a fundamental absorption band in the UV region (Fig. 2a). However, the diffuse reflectance spectra of CoPcS-TNP samples exhibit absorption bands in the 600–700 nm regions (Fig. 2b–e). The two maxima in the visible region correspond to the Q absorption bands originating from $\pi \rightarrow \pi^*$ transitions of CoPcS, which demonstrate that the absorption spectra of CoPcS-containing TiO_2 samples extend to the visible region. According to literature, the absorption bands at about 680 and 620 nm are attributed to monomeric and aggregated CoPcS species, respectively, Iliev et al. (1999).

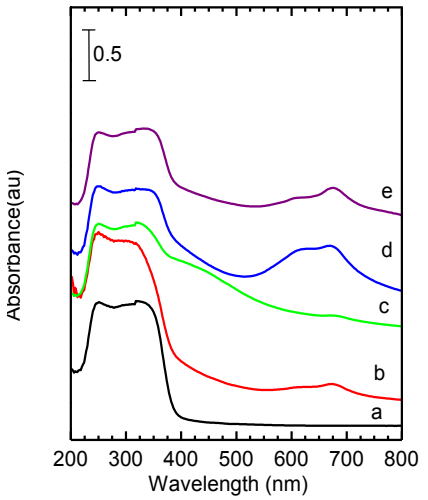

Fig. 2. Diffuse reflectance spectra of (a) TiO_2; (b) CoPcS-TNP (0.56); (c) CoPcS-TNP (1.12); (d) CoPcS-TNP (2.24); and (e) CoPcS-TNP (3.36).

3.3. Transmission electron microscopy

The TEM micrographs of pure TiO_2 and CoPcS-TNP (2.24) samples (Fig. 3) revealed that the samples consist of nanoparticles with diameters in the range from 7 to 10 nm. The particles are not agglomerated, which is advantageous to increase the photocatalytic efficiency of the prepared photocatalysts.

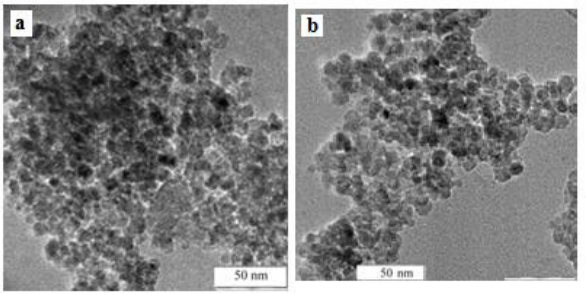

Fig. 3. TEM micrograph of (a) TiO_2 and (b) CoPcS-TNP (2.24).

3.4. Nitrogen physisorption

Textural and structural parameters of the CoPcS-TNP samples are summarized in table 1. Specific surface areas were calculated according to the BET method, pore volumes, and radii were derived from the desorption branch according to the BJH model. The specific surface areas of the CoPcS-containing TiO_2 materials are lower than that of pure TiO_2 suggesting that the CoPcS incorporation reduces the TiO_2 surface area.

Table. 1. Textural and structural parameters of the synthesized samples.

Sample	S_{BET} (m^2/g)	Pore radius (A°)	Pore volume (cm^3/g)
TiO_2	280	19	0.24
CoPcS-TNP (0.56)	133	35	0.26
CoPcS-TNP (1.12)	208	9	0.14
CoPcS-TNP (2.24)	141	38	0.29
CoPcS-TNP (3.36)	197	18	0.17

3.5. FTIR analysis

The presence of cobalt phthalocyanine species in CoPcS-TNP samples is detected by the band at about 1400 cm^{-1}, Karandikar et al. (2006). The intensity of the 1400 cm^{-1} band is weak, because the amount of CoPcS incorporated into TNP is low. The vibrations at about 670 cm^{-1} due to the sulfonic groups of CoPcS, Nabid et al. (2010), disappeared in the CoPcS-TNP samples, which is most likely due to the formation of TiO-SO_3^- bonding.

3.6. Photocatalytic degradation of 4-CP

Figure 4 show the photocatalytic degradation of 4-CP under various conditions. For this investigation, CoPcS-TNP (2.24) was used, because this sample has the highest photoactivity for degradation of 4-CP among synthesized photocatalysts. This high activity is not unexpected based on the comparison of the diffuse reflectance spectra of the samples (Fig. 2). Control experiments showed that the optimal dosage of photocatalyst is 0.3 g L^{-1}, and that a H_2O_2 concentration of 0.01 mol L^{-1} is adequate for photodegradation process of 4-CP. The results show that photodegradation efficiency is improved in the presence of the photocatalyst, H_2O_2, and visible light. Complete elimination of 4-CP is possible within 90 min optimizing all three factors. Thus, the synergetic effect of the sensitizer is demonstrated by the enhancement of the catalytic activities observed for the CoPcS-containing TiO_2 samples compared to pure TiO_2. Under visible light, the excited species in the system CoPcS-TNP is the dye molecule, but not the TiO_2 semiconductor. CoPcS has a strong absorption around 600–650 nm (Fig. 2), it has strong Q-band absorption and it can be excited. The excited CoPcS adsorbed on TiO_2 injects electrons to the conduction band (CB) of TiO_2. While the CB acts as a mediator for transferring electrons from the dye to substrate electron acceptors on the TiO_2 surface, the valence band (VB) remains unaffected. In the presence of TiO_2, the electron injection from the excited dye to the CB of TiO_2 is faster than the direct relaxation to the ground state. The activity of the photocatalyst may even be better by addition of hydrogen peroxide to the reactor (Fig. 4). Almost 50% of 4-CP was degraded within 90 min, when there is no H_2O_2 added. In the presence of H_2O_2, more hydroxyl radicals are produced compared to the conditions without using H_2O_2. This can be explained according to the below reaction.

$$H_2O_2 + O_2^{-\bullet} \rightarrow OH^{\bullet} + OH^- + O_2 \quad (1)$$

The faster hydroxyl radical formation is associated with the higher degradation rate.

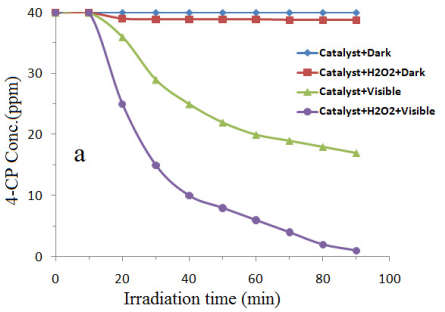

Fig. 4. Concentration changes of 4-CP at various conditions.

3.7. GC-MS analysis

Major reaction intermediates of 4-CP degradation containing carboxylic acid functional species characterized by GC-MS (Table 2). Presence of these intermediates can illustrate OH radicals role for degradation of 4-CP. The hydroxyl radicals attack 4-CP, converting them to chlorocatechol and then to chlorobenzoquinone. Subsequently, hydroxyl groups break the aromatic rings of chlorobenzoquinone, transferring them into simple acids as the final products, Chaliha et al. (2008).

Table 2. The main intermediates of 4-CP degradation determined by GC-MS.

Retention time (min)	Identified intermediate	Molecular formula
3.23	Methyl pyruvate	$H_3CCOCOOCH_3$
5.11	Methyl oxalate	$H_3COOCCOOCH_3$
7.36	Dimethyl malonate	$H_3COOCCH_2COOCH_3$
9.53	Methyl levulinate	$H_3CCOCH_2CH_2COOCH_3$
11.99	Benzoic acid, methyl ester	$C_6H_5COOCH_3$

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